

INSIGHTS INTO THE AQUEOUS HISTORY OF MARS FROM ACID-SULFATE WEATHERED PHYLLOSILICATES. P. I. Craig¹, D. W. Ming², E. B. Rampe³, R. V. Morris²; ¹Lunar and Planetary Institute, 3600 Bay Area Blvd, Houston, TX 77058; ²NASA Johnson Space Center, Houston, TX 77058; ³Aerodyne Industries, Jacobs JETS Contract, NASA JSC; craig@lpi.usra.edu

Introduction: Phyllosilicates on Mars are thought to have formed during Mars' earliest Noachian geologic era (~4.1-3.7 Ga) [e.g. 1]. Sulfate formation, on the other hand, requires more acidic conditions which are thought to have occurred later during Mars' Hesperian era (~3.7-3.0 Ga) [e.g. 1]. Therefore, regions on Mars where phyllosilicates and sulfates are found in close proximity to each other provide evidence for the aqueous conditions during this global transition.

Both phyllosilicates and sulfates form in the presence of water and thus give clues to the aqueous history of Mars and its potential for habitability. Phyllosilicates that formed during the Noachian era would have been weathered by the prevailing acidic conditions that define the Hesperian. Therefore, the purpose of this study is to characterize the alteration products of acid-sulfate weathered phyllosilicates in laboratory experiments, focusing on the Fe/Mg-smectites commonly identified on Mars [2]. We also compare our results to observations of phyllosilicates and sulfates on Mars in regions such as Endeavour Crater and Mawrth Vallis to understand the formation process of sulfates and constrain the aqueous history of these regions.

Experimental and Analytical Techniques: Powdered samples from the Clay Minerals Society's Source Clay Repository [Fe-smectite nontronite (NAu-1) and Mg-smectite saponite (SapCa-1)] were placed into Parr hydrothermal vessels with 0.01-1.0 M H₂SO₄ such that the water-rock ratio (WR) was ~50 or ~25. The vessels were then sealed and heated to 100°C for 72 hrs, then placed in a freezer until completely cooled. The liquid was gently pipetted off and the remaining solid sample was placed back into the oven at ~95°C until completely dry. Samples were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM/EDS), then placed into a dry N₂ glovebox [3] for two weeks to remove any adsorbed water prior to near-infrared (NIR) reflectance spectroscopic analysis.

Results and Discussion: XRD patterns of acid-treated nontronite showed a structural collapse of the phyllosilicate layers with increasing acid concentration by the decrease in intensity and shift of the 001 peak (Fig. 1). Bassanite (CaSO₄·0.5H₂O) formed in nontronite weathered in 0.1 M H₂SO₄ at WR = 50 from the extraction of interlayer Ca. While nontronite was more stable under lower WR conditions (001, 02ℓ and 060 peaks still present), the entire original sample was

eventually weathered to anhydrite (CaSO₄) and rhomboclase in 1.0 M H₂SO₄ at WR = 50 and gypsum (CaSO₄·2H₂O) and rhomboclase at WR = 25. This showed a change in the hydration state of the sulfates with changing acid concentration and water-rock ratio. A small "hump" feature is also evident at 2θ ~ 25-30° in the 1.0 M samples indicating an amorphous phase.

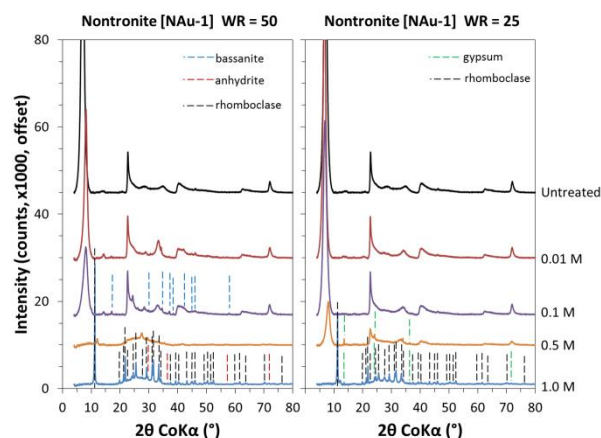


Figure 1: XRD patterns of acid-weathered nontronite.

Bassanite and anhydrite also formed in saponite treated at WR = 25 with hexahydrate (MgSO₄·6H₂O) and kieserite (MgSO₄·H₂O). However, only hexahydrate and kieserite formed in the WR = 50 samples (Fig. 2), again, showing differences in the hydration state of the resulting sulfate with changing acid concentration and water-rock ratio. Also, several silicate phases were identified in the WR = 25 samples, including quartz, diopside and K-feldspar. These were likely contaminants in the original sample whose relative abundance increased with the clay mineral dissolution.

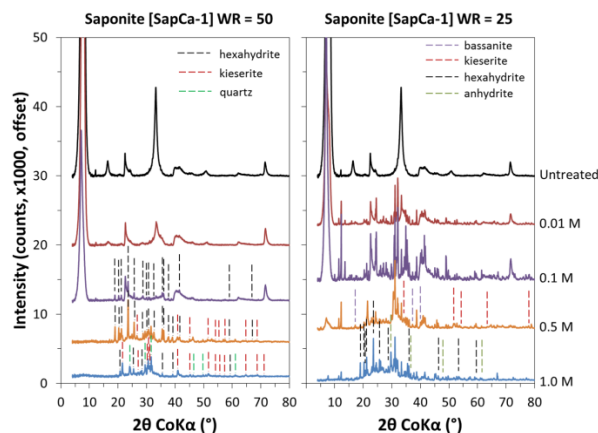


Figure 2: XRD patterns of acid-treated saponite.

Although no Ca-sulfates were identified by XRD in the saponite samples weathered under WR = 50, SEM/EDS analysis indicated the presence of Ca/S-rich particles in the sample (Fig. 3). This suggests the inter-layer Ca did weather out to form Ca-sulfates, but in quantities below the detection limit of XRD.

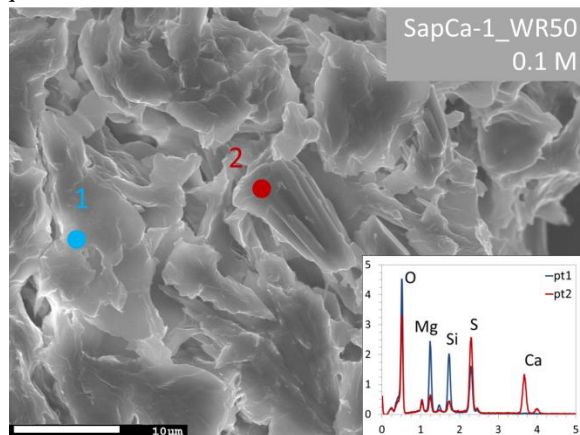


Figure 3: SEM/EDS of acid-weathered saponite.

Near-infrared reflectance spectra of the weathered samples showed a decrease in hydration band intensity and a shift or disappearance of the metal-OH bands (Figs. 4, 5) indicating the dehydration and dissociation of the octahedral layers with increased acid weathering. Additionally, the slope of the spectrum gradually became more negative with increasing acid weathering, indicative of the presence of sulfates [4].

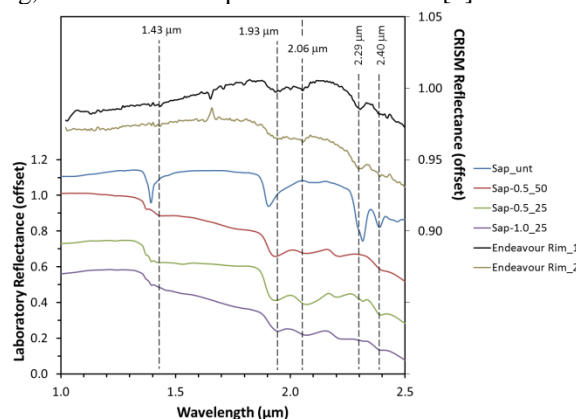


Figure 4: Comparison of NIR spectra of acid-treated saponite to spectra from around Endeavour Crater, Mars [11].

In summary, our experiments showed that interlayer Ca weathers out first [5] while the layered structure of the phyllosilicates (octahedral and tetrahedral layers) can remain intact. The leached Ca^{2+} combines with SO_4^{2-} to form Ca-sulfates. At higher acid concentrations, the tetrahedral and octahedral layers break down, resulting in amorphous phases, and sulfate compositions are then controlled by the octahedral cation.

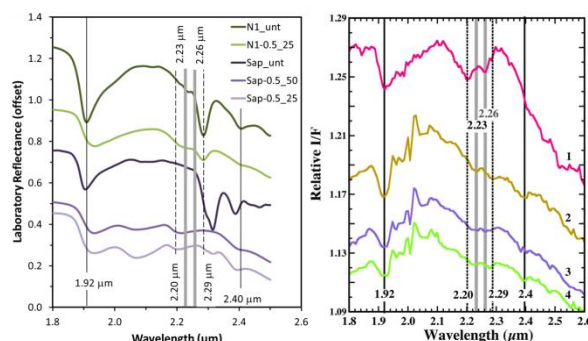


Figure 5: Comparison of NIR spectra of acid-treated nontronite and saponite (left) to spectra of phyllosilicates in Mawrth Vallis, Mars [8].

Implications for Mars: Phyllosilicates and sulfates have been identified in close spatial proximity to each other in several locations on Mars, including Gale Crater [6,7], Mawrth Vallis [8,9], and Endeavour Crater [10,11]. In the John Klein drill sample, ferroan saponite was identified by CheMin, along with Ca-sulfates anhydrite and bassanite [7]. The presence of Ca-sulfate veins in the drill sample was confirmed by ChemCam elemental analysis [12].

While several studies have shown that sulfates result from acid sulfate-weathered basalts [e.g., 13] it is possible that phyllosilicates that formed during Mars' earlier Noachian era would have been affected by the prevailing acidic conditions in the later Hesperian. Our experiments have shown that this type of weathering results in the formation of sulfates and could explain the observations of sulfates in close association with phyllosilicates. In fact, the spectral signature of our acid-weathered phyllosilicates is similar to those identified in the central peak and crater rim of Endeavour Crater (Fig. 4) and in Mawrth Vallis (Fig. 5) on Mars, suggesting these sulfates may be the acid-weathering product of the phyllosilicates.

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